



Particle partitioning potential of organic compounds is highest in the Eastern US and driven by anthropogenic water

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Abstract. Gas-phase water-soluble organic matter (WSOM_g) is ubiquitous in the troposphere. In the summertime, the potential for these gases to partition to particle-phase liquid water (H₂O_{ptcl}) where they can form secondary organic aerosol (SOA_{AQ}) is high in the Eastern US and low elsewhere, with the exception of an area near Los Angeles, CA. This spatial pattern is driven by mass concentrations of H₂O_{ptcl}, not WSOM_g. H₂O_{ptcl} mass concentrations are predicted to be high in the Eastern US, largely due to sulfate. The ability of sulfate to increase H₂O_{ptcl} is well established and routinely included in atmospheric models; however WSOM_g partitioning to this water and subsequent SOA formation is not. The high mass concentrations of H₂O_{ptcl} in the southeast (SE) US but not the Amazon may help explain why biogenic SOA mass concentrations are high in the SE US but low in the Amazon. Furthermore, during the summertime in the Eastern US, the potential for organic gases to partition into liquid water is greater than their potential to partition into organic matter (OM) because concentrations of WSOM_g and H₂O_{ptcl} are higher than semi-volatile gases and OM. Thus, unless condensed phase yields are substantially different (>~ order of magnitude), we expect that SOA formed through aqueous-phase pathways (SOA_{AQ}) will dominate in the Eastern US. These findings also suggest that H₂O_{ptcl} is largely anthropogenic and provide a previously unrecognized mechanism by which anthropogenic pollutants impact the amount of SOA mass formed from biogenic organic emissions. The previously reported estimate of the controllable fraction of biogenic SOA in the Eastern US (50 %) is likely too low.

1 Introduction

Liquid water is predicted to be the most abundant particle-phase species in the atmosphere, 2–3 times total aerosol dry mass globally (Liao and Seinfeld, 2005). However, chemical mechanisms employed in photochemical transport models largely underrepresent the impact of partitioning and oxidation reactions in aqueous media, in particular for organic species. This hinders development of effective strategies for air quality management and climate mitigation because important processes, feedbacks and anthropogenic influences are missing from model predictions.

Formation of secondary organic aerosol (SOA) through partitioning of semi-volatile products of gas-phase photochemical reactions into preexisting particulate organic matter (OM) (SOA_{gas}) is well established. For more than 20 years, empirical relationships developed from relatively dry SOA smog chamber studies conducted with little particle-phase liquid water (e.g., relative humidity (RH) < 20 %, Griffin et al., 1999; Ng et al., 2007) have provided critical data for atmospheric modeling of organic aerosol (Pankow, 1994; Odum et al., 1996; Seinfeld and Pankow, 2003). Despite studies of the effects of liquid water on the gas-particle partitioning of these semi-volatile products (Pun et al., 2002; Zuend and Seinfeld, 2012), atmospheric application of chamber-derived relationships describing SOA_{gas} remains problematic (Chang et al., 2010). This could be, at least in part, because derived empirical formulations do not include the potential for polar organic gases to partition to polar solvents such as water, and react in that medium to form low-volatility products. Parikh et al. (2011, 2012) find that when an Odum 2-product or volatility basis set (VBS) SOA model is applied to independent smog chamber studies

where relative humidity (RH) and particle-phase liquid water concentrations (H_2O_{ptcl}) are more typical of general atmospheric conditions, SOA parameterizations cannot reproduce observed amounts or trends in SOA mass (Parikh et al., 2011, 2012). In a series of experiments conducted in an outdoor chamber, accounting for gas-phase formation of water-soluble gases followed by partitioning into aerosol water was necessary to describe observed SOA mass accurately (Parikh et al., 2011, 2012). It is important to note available H_2O_{ptcl} is a function not only of RH but also of particle concentration and hygroscopicity (Zhou et al., 2011). Measurement of RH alone is not sufficient to determine H_2O_{ptcl} .

Gas-phase photochemistry oxidizes and fragments biogenic and anthropogenic volatile organic compounds (VOCs) resulting in the ubiquitous and abundant presence of small, water-soluble organic compounds (e.g., formic and acetic acids, glyoxal, methylglyoxal, acetone) (Spaulding et al., 2003). These compounds are too small to form SOA through traditional semi-volatile partitioning theory in atmospheric models (e.g., SOA_{gas}). However, it is now accepted that water-soluble compounds react in atmospheric waters (clouds, fogs and wet aerosols) to form SOA (Blando and Turpin, 2000; Ervens et al., 2011; Liu et al., 2012a). Evidence for SOA formation from gas followed by aqueous chemistry (SOA_{AQ}) is provided by laboratory experiments conducted at concentrations typical of atmospheric waters (e.g., with OH radicals and other reactants) that demonstrate formation of compounds found predominantly in the particle phase in the atmosphere: organic acids/salts (e.g., oxalate), high molecular weight compounds (HMWC) including oligomers, and sulfur- and nitrogen-containing organics (Carlton et al., 2006; Altieri et al., 2006, 2008; Guzman et al., 2006; Carlton et al., 2007; Noziere and Cordova, 2008; Volkamer et al., 2009; Galloway et al., 2009; Shapiro et al., 2009; De Haan et al., 2009a, b; El Haddad et al., 2009; Perri et al., 2009, 2010; Yao Liu et al., 2009; Liu et al., 2012b, c; Noziere et al., 2009, 2010; Yasmeen et al., 2010; Tan et al., 2010; Sun et al., 2010; Sareen et al., 2010; Grgic et al., 2010; Poulain et al., 2010; Zhang et al., 2010; Huang et al., 2011; Lee et al., 2011; Tan et al., 2012; Ortiz-Montalvo et al., 2012; Zarzana et al., 2012; Nguyen et al., 2012).

The analysis herein suggests that, as is the case for SOA_{gas} (Lane et al., 2008; Carlton et al., 2010b), anthropogenic pollution enhances the formation of biogenic SOA_{AQ} . We propose that this anthropogenic enhancement of biogenic SOA_{AQ} occurs because sulfur pollution increases the amount of H_2O_{ptcl} at a given relative humidity (RH) (Malm et al., 1994). In many locations including the Eastern US, SOA is predominantly formed from biogenic hydrocarbons (Lewis et al., 2004; Kleindienst et al., 2007; Ding et al., 2008). However, correlations between biogenic SOA mass and tracers of anthropogenic pollution are strong suggesting that anthropogenic pollution plays an important role in biogenic SOA formation (De Gouw and Jimenez, 2009). In fact anthropogenic aerosol water could potentially drive biogenic SOA

formation in high RH locations by providing the partitioning medium (H_2O_{ptcl}) for SOA_{AQ} formation. There is observational evidence suggesting enhancement of biogenic SOA mass derived from isoprene oxidation products when sulfate is present in the Eastern US (Chan et al., 2010), in particular when RH is high (Hatch et al., 2011). Anthropogenic pollution has been estimated to be responsible for roughly half of the biogenic SOA mass in the Eastern US (Carlton et al., 2010b). While anthropogenic H_2O_{ptcl} was estimated in those simulations, Gas-phase water-soluble organic matter ($WSOM_{\text{g}}$) partitioning and subsequent SOA_{AQ} formation in wet aerosol was not included. Thus the 50 % estimate is likely too low. Further, anthropogenic influences on H_2O_{ptcl} would also increase SOA derived from anthropogenic VOCs, which also oxidize to form gas-phase $WSOM_{\text{g}}$.

To explore potential drivers of spatial differences in observed SOA mass, we use a 3-dimensional photochemical transport model to predict mixing ratios of gas-phase organic compounds and mass concentrations of particulate species. We use these predictions to evaluate spatial trends in the overall solubility of organic gas-phase inventories, particle-phase concentrations of liquid water (H_2O_{ptcl}), and particulate OM. We use these predictions to estimate the chemical potential of organic gases to partition into liquid water. We also compare this potential (qualitatively) to the partitioning of semi-volatile organic gases into OM.

2 Methods

Version 4.7 of the Community Multiscale Air Quality (CMAQ) (www.cmascenter.org) model is applied to predict the photochemistry and transport of atmospheric trace species over the continental US for July 2003. Observational estimates during this time period indicate that secondary organic carbon is a substantial fraction of total particle carbon mass (Kleindienst et al., 2007).

2.1 CMAQ model simulations

CMAQ simulation details and inputs are described in detail elsewhere (Carlton et al., 2010b). Briefly, CMAQv4.7, with SOA formation (Carlton et al., 2010a) and aqueous-phase chemistry of sulfur, glyoxal and methylglyoxal in clouds (Carlton et al., 2008), is applied. The MM5 meteorology model, EPA's 2002 National Emissions Inventory (NEIv2) and the Biogenic Emission Inventory System (BEIS) (Pierce et al., 1998) are used to drive transport and develop anthropogenic and biogenic emissions, projected hourly for input to CMAQ with SMOKE (Houyoux et al., 2000). The SAPRC99 gas-phase chemical mechanism was used to simulate gas-phase photochemistry. The model domain is resolved horizontally with $36\text{ km} \times 36\text{ km}$ grid cells and vertically up to 100 mb with 14 vertical layers, with most resolution near the surface. Presented results are averages for July 2003.

Aerosol-free acidity is calculated in nmol m^{-3} from CMAQ predictions of Aitken and accumulation mode aerosol as

$$\text{H}^+ = 1000 \left[2 \frac{\text{SO}_4^{2-}}{96} + \frac{\text{NO}_3^-}{62} + \frac{\text{Cl}^-}{35} - \frac{\text{Na}^+}{23} - \frac{\text{NH}_4^+}{18} \right]. \quad (1)$$

The ion mass concentrations are calculated from the following CMAQ output species: $\text{SO}_4 = \text{ASO4I} + \text{ASO4J}$; $\text{NO}_3 = \text{ANO3I} + \text{ANO3J}$; $\text{Cl} = \text{ACLJ}$; $\text{Na} = \text{ANAJ}$; and $\text{NH}_4 = \text{ANH4I} + \text{ANH4J}$. A in the species name denotes aerosol, I the Aitken mode, and J the accumulation mode.

2.2 Water-soluble and semi-volatile gases

Organic gases listed in Table 1 are simulated in the CMAQ model when SAPRC is employed. Mixing ratios of each species are converted from ppb_v to ppb_vC , and mass concentrations are calculated in $\mu\text{g m}^{-3}$ using the ideal gas law and MM5-predicted air density. The sum of water-soluble gases simulated by CMAQ and shown in laboratory experiments to make SOA through aqueous-phase processes at concentrations typical of wet aerosol – glyoxal (Carlton et al., 2007), methylglyoxal (Tan et al., 2010), acetaldehyde (Li et al., 2011), methacrolein (El Haddad et al., 2009), phenols (Sun et al., 2010), acetone (Poulain et al., 2010), acetic acid (Tan et al., 2012) and glycolaldehyde (Perri et al., 2010) – is calculated as WSOM_g . Glycolaldehyde is not an explicit species in SAPRC99 and is counted as half of model species “RCHO”. It should be recognized that this summation is a lower bound estimate of WSOM_g with the potential to form SOA_{AQ} . Other water-soluble gases undoubtedly also form SOA_{AQ} . Formaldehyde, an abundant water-soluble gas, forms particle-phase hydroxymethanesulfonate in the presence of sulfur through aqueous-phase processes (Munger et al., 1984), but is not counted here. Only half of model species “RCHO” (C3 aldehydes and higher) was counted in the sum, but the uncounted RCHO mass will also likely form SOA_{AQ} to some degree similar to aldehydes that are considered (glyoxal, methylglyoxal, glycolaldehyde). Further, gas-phase isoprene photooxidation produces water-soluble epoxides (Paulot et al., 2009) recently detected in ambient particulate samples in the Southeast US (Budisulistiorini et al., 2013) but not included in this model simulation. The semi-volatile gas-phase species are the first and second products from isoprene, monoterpenes, sesquiterpenes, benzene, long-chain alkanes, toluenes and xylenes that form SOA in CMAQ (Carlton et al., 2010a) through semi-volatile partitioning (Odum et al., 1996) (SOA_{gas}). It should be noted that in reality some fraction of species included in the semi-volatile class would likely also partition to liquid water (Chang et al., 2010).

2.3 Methylglyoxal-equivalent solubility

In order to account for the combined effects of compound-specific water solubility and concentration, a solubility in-

dex for describing concentrations of all organic gases was adopted (e.g., not only water-soluble species for which laboratory experiments have been conducted, but all CMAQ-modeled species). Methylglyoxal is used as a reference compound because, as an oxidation product of both biogenic and anthropogenic hydrocarbons (Paulson and Seinfeld, 1992; Smith et al., 1999; Atkinson and Arey, 2003; Ham et al., 2006), it is found widely in urban and rural environments (Spaulding et al., 1999, 2003; Moortgat et al., 2002; Wang et al., 2002; Li and Yu, 2005; Ho et al., 2006). In this method, analogous to the propylene-equivalent concentration used in reactivity calculations (Chameides et al., 1992), a methylglyoxal-equivalent concentration is calculated for each organic species J in the SAPRC99 mechanism using values in Table 1.

$$\text{MGLY}_{\text{equiv}}(\text{J}) = [\text{C}_\text{J}] \frac{H_{\text{L},\text{J}}}{H_{\text{L},\text{MGLY}}}, \quad (2)$$

where C_J is the concentration of organic species J, $H_{\text{L},\text{J}}$ the Henry's law constant for species J, and $H_{\text{L},\text{MGLY}}$ the Henry's law constant for methylglyoxal. Henry's law constants are adjusted to hour-specific model-predicted temperature when appropriate (Table 1). $\text{MGLY}_{\text{equiv}}$ is the concentration of species J on a scale normalized to the solubility of methylglyoxal. $\text{MGLY}_{\text{equiv}}$ is the gas-phase mass concentration of methylglyoxal needed to generate an equal amount of partitionable (gas-to-aqueous) organic mass of species J. The concentration is calculated in $\mu\text{g m}^{-3}$ to investigate trends and patterns in gas-phase water-soluble organic matter (WSOM_g). In this context, if gas-phase organic species J had an atmospheric abundance of $10 \mu\text{g m}^{-3}$ and were twice as soluble as methylglyoxal, it would have a $\text{MGLY}_{\text{equiv}}$ concentration of $20 \mu\text{g m}^{-3}$; if the species were half as soluble as methylglyoxal, it would have a $\text{MGLY}_{\text{equiv}}$ concentration of $5 \mu\text{g m}^{-3}$. Because this solubility-based method accounts for a species' solubility as well as its atmospheric concentration, it provides an estimate of the relative contribution each organic species can make to the flux of gas-phase organic matter to aerosol water. It also provides a framework to compare spatial differences in the overall gas-phase organic solubility for a particular inventory.

2.4 Instantaneous aqueous partitioning potential

The overall potential for organic gas-to-liquid water partitioning is dependent not only on the concentration and water solubility of organic gases but also on the spatial and temporal co-location (or not) of liquid water. In this work we consider only particle-phase liquid water ($\text{H}_2\text{O}_{\text{ptcl}}$). The mass concentration of $\text{H}_2\text{O}_{\text{ptcl}}$ is predicted in CMAQ with ISORROPIA from water vapor mixing ratios and concentrations of inorganic species. In ISORROPIA, partitioning of inorganic species and atmospheric water between the gas phase and aerosol phase is calculated using relative humidity and molality of an aqueous binary solution of species containing

Table 1. Values used in $MGLY_{\text{equiv}}$ calculations for gas-phase organic species in the SAPRC99 gas-phase chemical mechanism as applied in CMAQv4.7.

Species name	mechanism	Species description	MW g mol ⁻¹	No. of C atoms	H ₁ mol atm ⁻¹
HCHO		formaldehyde	30	1	$3.2e03 \times \exp(6.8e03 \times T_{\text{fac}})$
CCHO		acetaldehyde	44	2	$1.4e01 \times \exp(5.6e03 \times T_{\text{fac}})$
RCHO		lumped C3+ aldehydes	58	3	4.20E+03
ACET		acetone	58	3	$3.0e01 \times \exp(4.6e03 \times T_{\text{fac}})$
MEK		ketones (and other non-aldehydes) with $k_{\text{OH}} < 5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ s}^{-1}$	72	3	$2.0e01 \times \exp(5.0e03 \times T_{\text{fac}})$
MEOH		methanol	32	1	2.20E+02
COOH		methyl hydroperoxide	48	1	$3.1e02 \times \exp(5.2e03 \times T_{\text{fac}})$
ROOH		lumped higher organic hydroperoxides	62	2	$3.1e02 \times \exp(5.2e03 \times T_{\text{fac}})$
GLY		glyoxal	58	2	3.60E+05
MGLY		methylglyoxal	72	3	3.20E+04
BACL		biacetyl	86	4	$7.4e01 \times \exp(5.7e03 \times T_{\text{fac}})$
PHEN		phenol	94	6	$1.9e03 \times \exp(7.3e03 \times T_{\text{fac}})$
CRES		cresols	108	7	8.20E+02
BALD		aromatic aldehydes (e.g., benzaldehyde)	106	7	$3.9e01 \times \exp(4.8e03 \times T_{\text{fac}})$
METHACRO		methacrolein	70	4	6.50E+00
MVK		methyl vinyl ketone	70	4	4.10E+01
ISOPROD		lumped isoprene products	70	4	4.10E+01
PROD2		ketones (and other non-aldehydes) with $k_{\text{OH}} > 5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-2} \text{ s}^{-1}$	100	4	4.10E+01
DCB1		reactive aromatic fragmentation products that do not undergo significant photodecomposition	58	3	8.20E+00
DCB2		reactive aromatic fragmentation products that photolyze with α -dicarbonyl-like action spectrum	72	4	8.20E+00
DCB3		reactive aromatic fragmentation products that photolyze with acrolein action spectrum	72	4	8.20E+00
HCOOH		formic acid	46	1	$8.9e03 \times \exp(6.1e03 \times T_{\text{fac}})$
CCO_OOH		peroxy acetic acid	76	2	$4.1e03 \times \exp(6.3e03 \times T_{\text{fac}})$
RCO_OH		higher organic acids	74	3	5.70E+03
CCO_OH		acetic acid	60	2	$8.4e02 \times \exp(5.3e03 \times T_{\text{fac}})$
RCO_OOH		higher organic peroxy acids	90	3	5.70E+03
ETHENE		ethene	28	2	4.70E-03
ISOPRENE		isoprene	68	5	2.80E-02
ALK1		alkanes (and other non-aromatics) that react only with OH, $k_{\text{OH}} < 5 \times 10^2 \text{ ppm}^{-1} \text{ min}^{-1}$ (primarily ethane)	30.1	2	$1.9E-03 \times \exp(2.3e03 \times T_{\text{fac}})$
ALK2		alkanes (and other non-aromatics) that react only with OH, $5 \times 10^2 < k_{\text{OH}} < 2.5 \times 10^3 \text{ ppm}^{-1} \text{ min}^{-1}$ (primarily propane and acetylene)	36.7	3	$0.0015 \times \exp(2.7e03 \times T_{\text{fac}})$
ALK3		alkanes (and other non-aromatics) that react only with OH, $2.5 \times 10^3 < k_{\text{OH}} < 5 \times 10^3 \text{ ppm}^{-1} \text{ min}^{-1}$	58.6	4	1.10E-03
ALK4		alkanes (and other non-aromatics) that react only with OH, $5 \times 10^3 < k_{\text{OH}} < 1 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	77.6	5	1.10E-03
ALK5		alkanes (and other non-aromatics) that react only with OH, $k_{\text{OH}} > 1 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	118.9	8	1.40E-04
ARO1		aromatics with $k_{\text{OH}} < 2 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	98.6	7	$1.5e-01 \times \exp(4.0e03 \times T_{\text{fac}})$
ARO2		aromatics with $k_{\text{OH}} > 2 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	118.7	8	$1.9e-01 \times \exp(4.0e03 \times T_{\text{fac}})$
OLE1		alkenes (other than ethene) with $k_{\text{OH}} < 7 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	72.3	6	4.70E-03
OLE2		alkenes with $k_{\text{OH}} > 7 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$	75.8	6	4.70E-03
TRP1		terpenes	136	10	4.90E-02
SESQ		sesquiterpenes	204	15	4.90E-02
BENZENE		benzene	78	6	$1.6e-01 \times \exp(4.1e03 \times T_{\text{fac}})$

$$T_{\text{fac}} = (298 - \text{Temp}) / (298 \times \text{Temp})$$

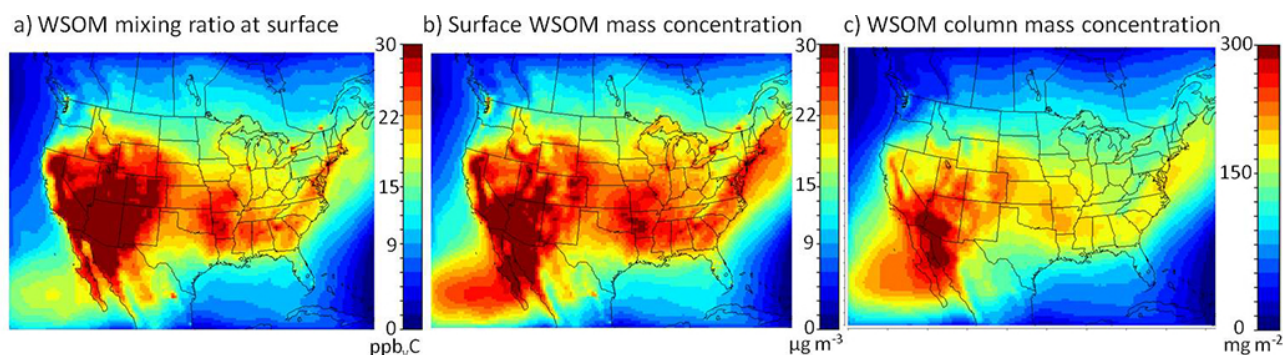


Fig. 1. (a) Sum of gas-phase CMAQ water-soluble organic gases shown in lab experiments to make SOA_{AQ} : glyoxal (Carlton et al., 2007), methylglyoxal (Tan et al., 2010), acetaldehyde (Li et al., 2011), phenols (Sun et al., 2010), acetone (Poulain et al., 2010), acetic acid (Tan et al., 2012), methacrolein (El Haddad et al., 2009) and glycolaldehyde (Perri et al., 2010). Note that glycolaldehyde is not an explicit species in SAPRC99 (used in this simulation) and is counted as half of model species “RCHO”. For the mixing ratio (a), all gases are presented in $\text{ppb}_v\text{-C}$. The mass concentrations in (b) and (c) are converted from the molar ratios using the ideal gas law. Values are July 2003 averages.

sulfate, nitrate, chlorine, sodium and ammonium (Nenes et al., 1999). The partitioning potential of WSOM_g to liquid water is calculated with a thermodynamic equilibrium assumption as is done for gas-phase organic species that partition to OM (Pankow, 1994). The potential is calculated here:

$$P_{\text{WSOMP}(J)} = [C_J][C_{\text{H}_2\text{O}}] \frac{H_J}{H_{\text{MGLY}}} \phi_J \\ = \text{MGLY}_{\text{equiv}}[C_{\text{H}_2\text{O}}] \phi_J, \quad (3)$$

where C_J is the concentration of organic species J ($\mu\text{g m}^{-3}$) and $C_{\text{H}_2\text{O}}$ is the liquid water concentration ($\text{H}_2\text{O}_{\text{ptcl}}$) ($\mu\text{g m}^{-3}$). ϕ_J is referred to as the SOA_{AQ} -forming potential, analogous to incremental reactivity in ozone studies (Chameides et al., 1992). ϕ_J represents the likelihood organic mass will remain in the condensed phase after partitioning, for example by being transformed into low-volatility products through radical and non-radical reactions (Ervens et al., 2011). ϕ_J depends on a variety of factors including the presence of other aqueous species/reactants (e.g., OH radicals, NH_3), yields of low-volatility products from such aqueous reactions and local meteorology (e.g., temperature and RH). Values of ϕ_J are not currently known and are likely not constant. To explore sensitivity of the partitioning potential to ϕ , we perform two calculations with constant ϕ values: the first with ϕ set to 1 and another with ϕ set to 0.1 for all species. These assumptions are not correct and represent non-trivial limitations of the framework, but regardless the partitioning potential is useful as an index that identifies areas where SOA_{AQ} is likely to be important. In assessing this partitioning potential, the relative importance of one organic species to another will depend not only upon the relative concentrations of the compound in the $\text{MGLY}_{\text{equiv}}$ index but also upon the liquid water content of the air mass. For this reason, a highly soluble species with a large concentration will not necessarily be an important precursor if not co-located with $\text{H}_2\text{O}_{\text{ptcl}}$ in space and time.

2.5 Limitations

There are uncertainties when calculating partitioning potentials and comparing pathways. First, the degree to which CMAQ accurately represents particle-phase liquid water mass is not well understood. CMAQ might underpredict $\text{H}_2\text{O}_{\text{ptcl}}$ because ISORROPIA, the thermodynamic partitioning model implemented in CMAQ and employed to predict particle-phase liquid water, includes only inorganic species. In laboratory studies, organic compounds ubiquitous in the troposphere (e.g., methylglyoxal and acetaldehyde) increase particle hygroscopicity (Sareen et al., 2013), and particle-phase organic material is reported to contribute to $\text{H}_2\text{O}_{\text{ptcl}}$ in several locations (Dick et al., 2000; Canepari et al., 2013). Second, it is well established that CMAQv4.7 underpredicts secondary organic aerosol mass (Carlton et al., 2010a; Carlton and Baker, 2011). The uncertainties in $\text{H}_2\text{O}_{\text{ptcl}}$, OM, WSOM_g and semi-volatile gas-phase species constitute the major limitations of this assessment.

Organic species are often found in the aerosol aqueous phase at concentrations higher than predicted by Henry's law (e.g., glyoxal; Kroll et al., 2005). Nevertheless, Henry's law constants are predictors of organic gas-to-aqueous partitioning and therefore useful in a “partitioning potential” calculation. The assumption of constant $\phi_J = 1$ or 0.1 for all organic species is not correct. Appropriate values for ϕ are not well understood. The results herein provide a framework to identify species, locations and times where SOA_{AQ} formation is likely to be important, and further investigation is warranted.

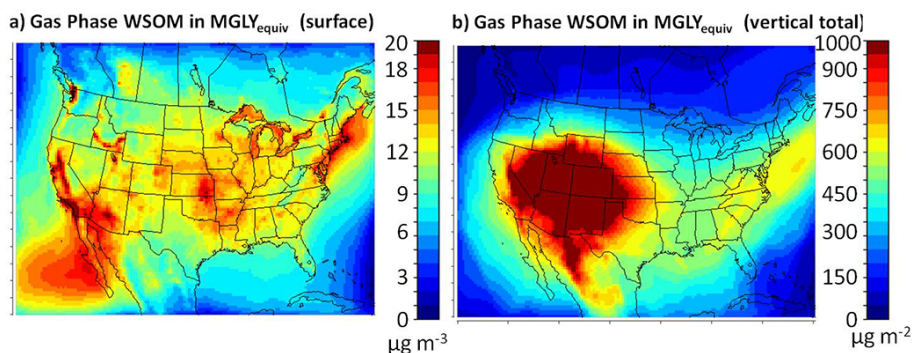


Fig. 2. MGLY_{equiv} mass concentrations for gas-phase water-soluble organic matter (WSOM) at the surface (a) and for the model column (surface to 100 mb) (b). Note that all species included in Table 1 are used in the calculation of MGLY_{equiv}. Values are July 2003 averages.

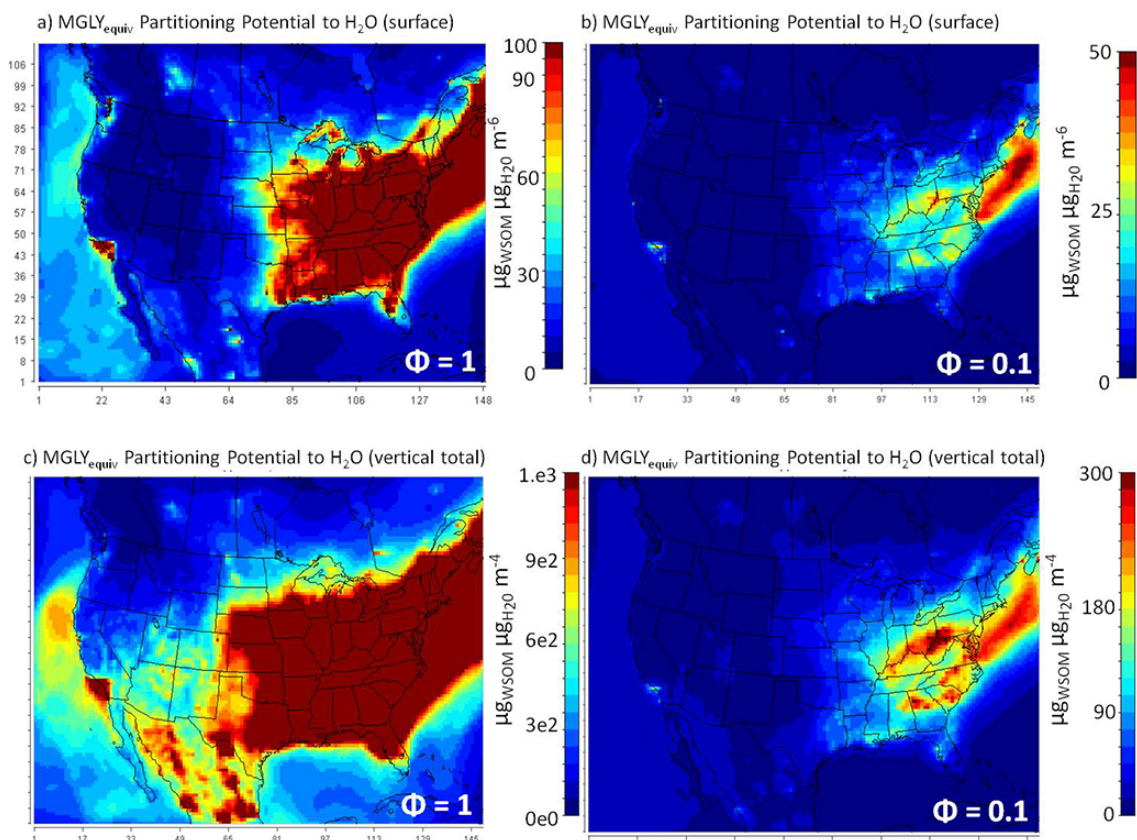


Fig. 3. Instantaneous partitioning potential for gas-phase water-soluble organic matter (WSOM) as MGLY_{equiv} to partition to particle phase liquid water at the surface for $\phi = 1$ (a) and $\phi = 0.1$ (b), and for the model column (up to 100 mb) for $\phi = 1$ (c) and $\phi = 0.1$ (d). Values are July 2003 averages.

3 Results

3.1 Ubiquity of water-soluble organic gases

In the summertime, throughout the troposphere over the continental US water-soluble organic gases, demonstrated to form SOA in laboratory experiments through aqueous-phase chemistry, are ubiquitous (Fig. 1). This finding is consis-

tent with a variety of ambient measurements that indicate WSOM_g is abundant (Chebbi and Carlier, 1996; Nolte et al., 1999; Hennigan et al., 2009). At the surface, mass concentrations of WSOM_g in MGLY_{equiv} are high throughout the US, typically $>20 \mu\text{g m}^{-3}$ (Fig. 2). MGLY_{equiv} concentrations suggest organic gas-phase inventories are soluble throughout the US (Fig. 2a). When the entire model column is considered (up to 100 mb), mass concentrations of WSOM

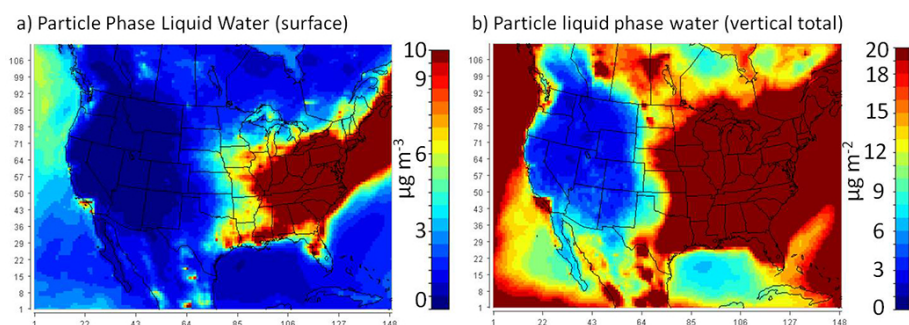


Fig. 4. (a) Particle-phase liquid water concentrations at the surface (0–34 m) and (b) for the model column (surface up to 100 mb). Values are July 2003 averages.

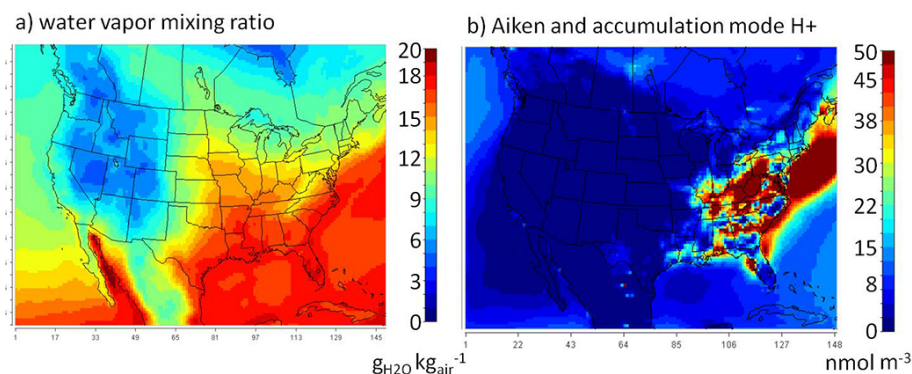


Fig. 5. Water vapor mixing ratio (a) and aerosol-free acidity (b) at the surface averaged for July 2003.

in $\text{MGLY}_{\text{equiv}}$ are ubiquitously large (typically $> 500 \mu\text{g m}^{-2}$) and greatest in the western US ($> 1 \text{ mg m}^{-2}$) (Fig. 2b). Tropospheric gas-phase organic inventories over the continental US are highly water-soluble, whether evaluated in mixing ratios, mass concentrations or $\text{MGLY}_{\text{equiv}}$.

3.2 WSOM aqueous partitioning potential is high in the Eastern US

The instantaneous potential for gas-phase water-soluble organic matter to partition to particle-phase liquid water is large in surface air in the Eastern US and small elsewhere, with the exception of an area near Los Angeles, CA (Fig. 3 and Supplement) and “hot spots” in Mexico. A similar trend is observed when the entire column is considered. Unlike water-soluble gas concentrations (WSOM_g , $\text{MGLY}_{\text{equiv}}$), this “liquid water partitioning potential” is not spatially ubiquitous. This phenomenon is explained by spatial patterns in $\text{H}_2\text{O}_{\text{ptcl}}$ mass concentrations (Fig. 4). The abundance of $\text{H}_2\text{O}_{\text{ptcl}}$ is a function of the mixing ratio of water vapor in the atmosphere and the concentration and hygroscopicity of the aerosol. Water vapor mixing ratios are highest in the Eastern US, as are aerosol-free acidity concentrations (Fig. 5). The abundance of aerosol-free acidity in the Eastern US is influenced to a large degree by anthropogenic SO_2 emissions and the subsequent sulfate aerosol mass concentrations. Other contributors

to aerosol acidity (NO_3 , Cl) do not contribute substantially to un-neutralized H^+ and are not visible when plotted at the same scale in Fig. 6 for this simulation. The total aerosol-free acidity ($\sim 50 \text{ nmol m}^{-3}$) is less than the sulfate acidity ($\sim 200 \text{ nmol m}^{-3}$) due to the neutralization of ammonium. In these simulations, particle-phase acidity and the resulting H_2O uptake are anthropogenic in surface air over the continental US.

The simulated increase in partitioning potential when liquid water is available is consistent with ambient observations. Hennigan et al. (2008, 2009), and Sorooshian et al. (2010), find that when liquid water is available, the fraction of WSOM found in the particle-phase increases with increasing sub-saturated relative humidity (Hennigan et al., 2008, 2009; Sorooshian et al., 2010). Particle-phase WSOM also increases with increasing aerosol hygroscopicity (Sorooshian et al., 2010). This work suggests that because gas-phase WSOM is ubiquitous and $\text{H}_2\text{O}_{\text{ptcl}}$ is not, the availability of particle-phase liquid water caused by anthropogenic influences is the limiting factor in SOA_{AQ} formation over the continental US.

CMAQ-estimated polar, water-soluble gases are more abundant than semi-volatile organic gases and particle-phase liquid water is more abundant than dry organic aerosol mass in the summertime over the US. In many locations, in

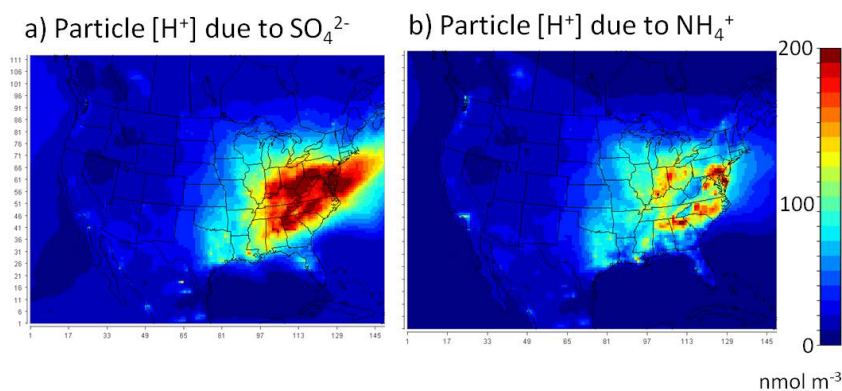


Fig. 6. Particle-phase H^+ concentration due to sulfate (a) and the neutralizing concentration of ammonium (b). Values are averaged for July 2003.

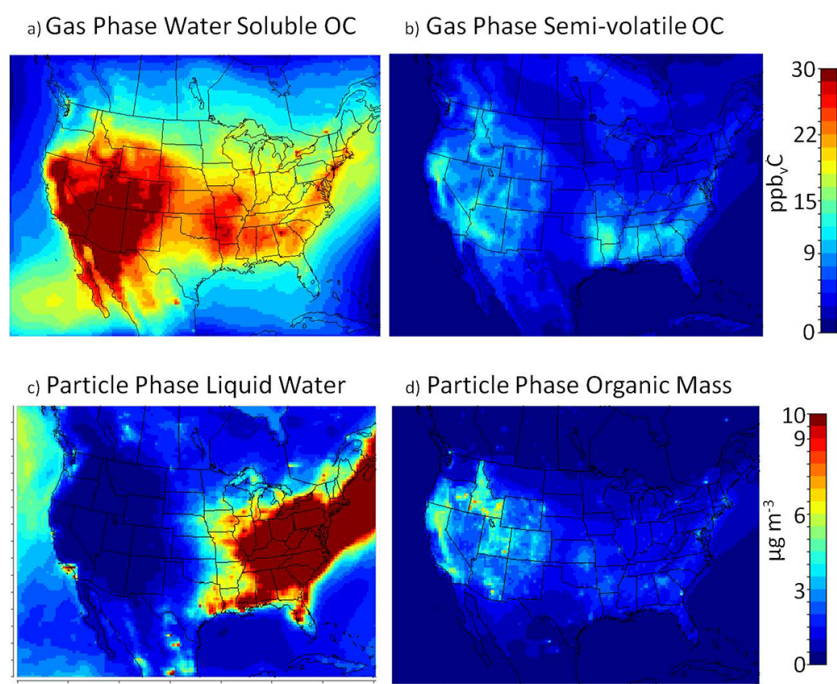


Fig. 7. Qualitative comparison of the potential of water-soluble gases to partition to aerosol water (left) versus the potential of semi-volatile gases to partition particle-phase organic matter (right). All values are averaged for July 2003. Included are species for which laboratory experiments have been conducted, as in Fig. 1.

particular the eastern US, the chemical potential for aqueous partitioning (water-soluble gases to particle liquid water) appears to be greater than the potential for semi-volatile gases to partition to dry OM (Fig. 7). Thus, unless condensed phase yields of low-volatility products are substantially different (order of magnitude), we expect that SOA_{AQ} will be more important than SOA_{gas} in the Eastern US. It also seems that the overall geographic distribution of SOA_{gas} and SOA_{AQ} are driven predominantly by the geographic distribution of OM and $\text{H}_2\text{O}_{\text{ptcl}}$, which are spatially limited compared to the organic precursor gases.

3.3 Biogenic SOA is controllable

Insights gained from this work lead us to hypothesize that biogenic SOA is abundant in the Southeastern US (Kleindienst et al., 2007; Lewandowski et al., 2007; Hennigan et al., 2008, 2009; Kleindienst et al., 2010) but lower in the Amazon (Pöschl et al., 2010; Martin et al., 2010) because $\text{H}_2\text{O}_{\text{ptcl}}$ concentrations are high (and anthropogenic) in the SE US but low in the Amazon. Global predictions of $\text{H}_2\text{O}_{\text{ptcl}}$ by Liao and Seinfeld (2005) support this idea. This work suggests SO_2 pollution contributes to biogenic SOA mass concentrations in the eastern US through mechanisms not currently

accounted for in atmospheric models. Carlton et al. (2010b) previously estimated that anthropogenic pollution accounts for approximately half of biogenic SOA (SOA formed from biogenic hydrocarbons) in the eastern US. The framework herein identifies another mechanism by which anthropogenic pollution can facilitate “biogenic” SOA production, and suggests that previous estimates of the controllable fraction of biogenic SOA are too low.

4 Conclusions

Over the continental US water-soluble organic gases demonstrated to form SOA through aqueous-phase chemistry are ubiquitous in the troposphere during the summertime. In the Eastern US, the potential for organic gases to partition to liquid water is greater than the potential to partition to particle-phase organic matter. Partitioning of organic material to the condensed phase is limited by controllable mass concentrations of $\text{H}_2\text{O}_{\text{ptcl}}$. Future investigations regarding the controllable fraction of organic aerosol should include simultaneous explicit phase partitioning of water-soluble and semi-volatile gases to condensed organic matter and liquid water.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys.net/13/10203/2013/acp-13-10203-2013-supplement.pdf>.

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